PA. .NT COOPERATION TREATY

From the INTERNATIONAL BUREAU

PCT

NOTIFICATION OF ELECTION

(PCT Rule 61.2)

To:

United States Patent and Trademark Office
(Box PCT)
Crystal Plaza 2
Washington, DC 20231
ÉTATS-UNIS D'AMÉRIQUE

in its capacity as elected Office

Date of mailing (day/month/year) 09 February 1999 (09.02.99)	
International application No. PCT/US98/12295	**Applicant's or agent's file reference** B1029/7001WO
International filing date (day/month/year) 12 June 1998 (12.06.98)	**Priority date** (day/month/year) 12 June 1997 (12.06.97)
Applicant ILYASHENKO, Victor, M.	

1. The designated Office is hereby notified of its election made:

[X] in the demand filed with the International Preliminary Examining Authority on:

11 January 1999 (11.01.99)

[ ] in a notice effecting later election filed with the International Bureau on:

2. The election [X] was

[ ] was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

The International Bureau of WIPO **34, chemin des Colombettes** **1211 Geneva 20, Switzerland**	Authorized officer C. Carrié
Facsimile No.: (41-22) 740.14.35	Telephone No.: (41-22) 338.83.38

PATENT COOPERATION TREATY

REC'D 0 3 SEP 1999
WIPO PCT

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference	FOR FURTHER ACTION	See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)
B1029/7001WO		
International application No.	International filing date *(day/month/year)*	Priority date *(day/month/year)*
PCT/US98/12295	12/06/1998	12/06/1997
International Patent Classification (IPC) or national classification and IPC G02B6/18		
Applicant BOSTON OPTICAL FIBER, INC. et al.		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of 8 sheets, including this cover sheet.

   ☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

   These annexes consist of a total of 15 sheets.

3. This report contains indications relating to the following items:

   - I ☒ Basis of the report
   - II ☐ Priority
   - III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
   - IV ☐ Lack of unity of invention
   - V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations suporting such statement
   - VI ☐ Certain documents cited
   - VII ☒ Certain defects in the international application
   - VIII ☒ Certain observations on the international application

Date of submission of the demand	Date of completion of this report
11/01/1999	01.09.99
Name and mailing address of the international preliminary examining authority: European Patent Office D-80298 Munich Tel. (+49-89) 2399-0 Tx: 523656 epmu d Fax: (+49-89) 2399-4465	Authorized officer Lord, R Telephone No. (+49-89) 2399 2580

Form PCT/IPEA/409 (cover sheet) (January 1994)

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/US98/12295

I. Basis of the report

1. This report has been drawn on the basis of (*substitute sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments.*):

Description, pages:

1-3,9-11,13-23	as originally filed			
8,12	as received on	07/06/1999	with letter of	03/06/1999
4-7,7a	as received on	16/08/1999	with letter of	13/08/1999

Claims, No.:

9-38	as originally filed			
1-8,39-73	as received on	16/08/1999	with letter of	13/08/1999

Drawings, sheets:

1/2,2/2	as originally filed

2. The amendments have resulted in the cancellation of:

☐ the description, pages:
☐ the claims, Nos.:
☐ the drawings, sheets:

3. ☒ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

see separate sheet

4. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims 1-71,73
	No:	Claims 72
Inventive step (IS)	Yes:	Claims 1-56
	No:	Claims 57-73
Industrial applicability (IA)	Yes:	Claims 1-73
	No:	Claims

2. Citations and explanations

see separate sheet

VII. Certain defects in the international application

The following defects in the form or contents of the international application have been noted:

see separate sheet

VIII. Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

see separate sheet

Concerning Section I

1. The amended claims 1, 45, 57 and 73 no longer define that the core and the sheathing are coaxial. Since this feature appeared in all of the original independent claims and the corresponding statements of the invention, it must be concluded that it represents an essential feature of the invention. Its deletion therefore represents an extension of the subject-matter of the application beyond the disclosure of the application documents as filed, contrary to the requirements of Article 34(2)(b) PCT.

2. The amended claim 72 and the corresponding citation on page 7 include the feature that the core dopant concentration does not exceed 7.9 %wt. This feature has no basis in the original application documents, so that the resultant subject-matter extends beyond the content of the application as originally filed, contrary to the requirements of Article 34(2)(b) PCT. The example on page 22 referred to by the applicant cannot be considered to provide a basis for the amendment, since it discloses only the value of 7.9 %wt, but does not disclose that this should be a limiting value of a range for this parameter (i.e. it does not disclose values below 7.9 %wt).

Concerning Section V

Claims 1, 31, 45, 49 and 53

Subject to the comments in section VIII, paragraph 2, of this Examination Report, these claims define devices and methods incorporating the concept of including an index-depressing dopant in the sheathing of a graded index article in which the core and sheathing are of the same polymeric material, the core including also an index-raising dopant. The use of the index-depressing sheathing dopant results in an adequate index difference being achieved without requiring concentrations of the core dopant that lead to increased attenuation. The available prior art documents provide no suggestion of this development, so that these claims meet the requirements of Article 33(2) and (3) PCT.

Claims 2 to 30, 32 to 44, 46 to 48, 50 to 52 and 54 to 56

These claims define specific embodiments of the inventive concept discussed above, and thus (again subject to the comments in section VIII of this Examination Report) meet the requirements of Article 33(2) and (3) PCT.

Claim 57

The paper "High-Bandwidth Graded-Index Polymer Optical Fiber" Journal of Lightwave Technology, vol. 13, no. 7, 1 July 1995, pages 1475-1489 by Koike, Y et al, hereinafter referred to as D1, describes in section III. A, in the passage entitled "Formation of Graded-Index", the fabrication of a plastic optical preform article comprising a polymer sheathing (polymer tube), including a sheathing polymer (MMA), and a polymeric core, polymerised within the sheathing and including a core polymer. The core and sheathing are clearly at least partially transparent at at least one wavelength. As depicted in figure 3, the refractive index at the central axis of the core is higher than that of the sheathing. The preform of the present claim 57 is thus distinguished from this known preform only in that the sheathing includes a plasticiser. The skilled person in the technical field of polymers is however well aware that plasticisers can be advantageously introduced into a polymer in order to improve its mechanical properties, so that this modification would be obvious. The argument raised by the applicant that the skilled person would believe that the incorporation of conventional plasticisers would lead to performance degradation, so that he would not consider this modification, does not affect this argument, since the claim does not define that these detrimental effects are overcome, let alone how they are overcome. Therefore the subject-matter of this claim does not involve an inventive step, so that the claim does not meet the requirements of Article 33(3) PCT.

Claims 58 to 70

These claims define either features which are also present in the preform of D1 (claims 58 to 64, 66 and 67) or features which are well-known in the technical field such that their introduction into the preform discussed above would be obvious to the skilled person (claims 65 and 68 to 70). Therefore the subject-matter of these claims also does not involve an inventive step, so that they do not meet the requirements of Article 33(3) PCT.

Claim 71

The method described in the section of D1 cited above comprises forming a polymeric preform rod comprising a polymeric sheathing and a polymeric core coaxially disposed within the sheathing, the polymeric core having a gradient in refractive index in a specific direction, as depicted in figure 3. The following section, entitled "Fiber Fabrication", describes the fabrication of a gradient index plastic optical fibre by hot drawing the preform rod at a controlled speed. As shown in figure 12 of D1, the resultant fibre conducts light with an attenuation less than 500 dB/km at at least one wavelength. The method of the present claim is thus distinguished from that of D1 only by the feature that the draw rate is at least 3 m/min. The skilled person in the field of fibre drawing is however aware that a high draw rate is desirable for cost reasons. The specification of a minimum value for a parameter which the skilled person knows should be maximised cannot be considered to involve an inventive step. The applicant's argument that the prior art documents do not teach how to achieve this increased draw rate is in itself correct, but is not relevant to the issue of inventive step in the present claim, since the claim also does not define how this is achieved, merely that it is achieved. Therefore this claim also does not meet the requirements of Article 33(3) PCT.

Claim 72

The document EP-A-0 606 598 (hereinafter referred to as D2) describes in example 3 a plastic optical preform article comprising a polymeric sheathing (tube cladding) which includes a sheathing polymer (polymerised HFIP2FA) and a polymeric core, coaxially disposed with the sheathing (implicit) and including a core polymer (polymerised HFIP2FA) and a core dopant (dibutyl phthalate) having a refractive index greater than the core polymer (see e.g. claim 2). The feed ratio of the two components of the core is indicated as 10/1, so that the overall core dopant concentration is less than 12 wt% (see Section I of this Examination Report). From figures 7 and 8 it is clear that the sheathing and core are at least partially transparent at at least one wavelength and that the refractive index at the central axis of the core exceeds that of the sheathing. As indicated at page 3, lines 37-38 the fibres produced using the preform of D2 have an attenuation less than 500 dB/km. Thus the preform of D2 includes all the technical features of the present claim 72, so that the subject-matter of the claim is not new. Therefore the claim does not meet the requirements of Article 33(2) PCT.

Claim 73

The article defined in this claim is distinguished from that of D2 described above only in that the operating temperature is defined to be at least 40°C. This represents merely an obviously desirable property, and cannot therefore be considered to involve an inventive step. The applicant's arguments that the prior art documents do not teach how to achieve this operating temperature are, for reasons analogous to those given above with respect to claim 71, also not considered to be relevant to this issue, since this claim also does not define how the desired property is achieved. Therefore the claim does not meet the requirements of Article 33(3) PCT.

Concerning Section VII

1. The independent claims do not meet the requirements of Rule 6.1(b)(i) and (ii) PCT that they should distinguish those technical features which are known in combination from the prior art from those technical features which, in combination with those of the prior art, it is desired to protect. In this context it would appear that the document D1 referred to above represents the most relevant prior art for claims 1, 31, 45, 49, 53, 57 and 71, and that the document D2 represents the most relevant prior art for claims 72 and 73.

2. The description of page 5, lines 12 and 13, indicates that the subject-matter of the original claim 45 forms part of the invention, although this claim has now been deleted. The description is thus not consistent with the claims, contrary to the requirements of Rule 5.1(a)(iii) PCT.

Concerning Section VIII

1. The use of seven independent claims in the device category and two in the method category, these claims being of partially overlapping scope, and in some cases being distinguished from the prior art by different features, renders the nature of the claimed invention unclear, so that the claims do not meet the requirements of Article 6 PCT. The different distinguishing features also suggest a

lack of unity of invention, contrary to the requirements of Rule 13.1 PCT.

2. The description of the present application suggests that the invention relates to the technical problem that in graded index plastic optical articles in which the core and sheathing (cladding) are formed of the same polymeric material, the core index being increased by the incorporation of an index-raising dopant, the high concentration of the dopant required to achieve an adequate index difference relative to the sheathing can lead to increased attenuation, and that this problem is solved by introducing an index-depressing dopant into the sheathing, so that the same index difference can be achieved with a lower core dopant concentration. The present independent claims 1, 31, 45, 49 and 53 do not however clearly define all the technical features which are essential to this invention, so that they do not meet the requirements of Article 6 PCT. The essential features which are considered to be missing in one or more of the cited claims are (i) that the core polymer and sheathing polymer are the same, (ii) that the core contains an index-raising dopant, and (iii) that the sheathing contains an index-depressing dopant. The feature (i) does not appear in any of the listed claims. The feature (ii) does not appear in claims 1 and 31, since no definition is given as to how the index gradient is achieved. The feature (iii) does not appear in claims 31, 45, 49 and 53, since claim 31 does not define the nature of the sheathing dopant, and since claims 45, 49 and 53 define only (and in obscure terms) that the index of the sheathing is lower than that of the core, but not the manner in which this is achieved. Obviously these features are also missing, at least in part, from the claims discussed in section V above.

3. Claims 59 to 64 define only uses for which the preform might be used, such that they cannot be considered to clearly define any features of the preform itself. These claims are therefore also unclear, contrary to the requirements of Article 6 PCT.

PATENT COOPERATION TREATY

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference	**FOR FURTHER ACTION** see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.	
B1029/7001WO		
International application No.	International filing date *(day/month/year)*	(Earliest) Priority Date *(day/month/year)*
PCT/US 98/ 12295	12/06/1998	12/06/1997
Applicant		
BOSTON OPTICAL FIBER, INC. et al.		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 3 sheets.

[X] It is also accompanied by a copy of each prior art document cited in this report.

1. [ ] **Certain claims were found unsearchable** (see Box I).

2. [ ] **Unity of invention is lacking** (see Box II).

3. [ ] The international application contains disclosure of a **nucleotide and/or amino acid sequence listing** and the international search was carried out on the basis of the sequence listing
   - [ ] filed with the international application.
   - [ ] furnished by the applicant separately from the international application,
     - [ ] but not accompanied by a statement to the effect that it did not include matter going beyond the disclosure in the international application as filed.
   - [ ] Transcribed by this Authority

4. With regard to the **title,**
   - [X] the text is approved as submitted by the applicant
   - [ ] the text has been established by this Authority to read as follows:

5. With regard to the **abstract,**
   - [X] the text is approved as submitted by the applicant
   - [ ] the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this International Search Report, submit comments to this Authority.

6. The figure of the **drawings** to be published with the abstract is:
   Figure No. 1
   - [X] as suggested by the applicant.
   - [ ] because the applicant failed to suggest a figure.
   - [ ] because this figure better characterizes the invention.
   - [ ] None of the figures.

INTERNATIONAL SEARCH REPORT

Inter[redacted]al Application No
PCT/[redacted]S 98/12295

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 G02B6/18 B29D11/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 G02B B29D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	CA 2 188 215 A (FURUKAWA ELECTRIC CO LTD) 21 April 1997 see claim 1 ---	1
A	EP 0 615 141 A (KOIKE YASUHIRO) 14 September 1994 see claims 1-4 see page 5; table 2 see page 6, line 11 - line 40 see page 7, line 20 - line 49; figure 5 ---	1
A	EP 0 606 598 A (HOECHST CELANESE CORP ;KOIKE YASUHIRO (JP)) 20 July 1994 see claims 1-6,13-23 see page 7, line 1 - line 24 ---	1
	-/--	

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
26 August 1998	09/09/1998

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Depijper, R

1

Form PCT/ISA/210 (second sheet) (July 1992)

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
A	ISHIGURE T ET AL: "HIGH BANDWIDTH AND HIGH NUMERICAL APERTURE GRADED-INDEX POLYMER OPTICAL FIBRE" ELECTRONICS LETTERS, vol. 30, no. 14, 7 July 1994, pages 1169-1171, XP000461190 * whole article *	1
A	KOIKE Y ET AL: "HIGH-BANDWITH GRADED-INDEX POLYMER OPTICAL FIBER" JOURNAL OF LIGHTWAVE TECHNOLOGY, vol. 13, no. 7, 1 July 1995, pages 1475-1489, XP000597673 see page 1477; tables 1,2	1
P,A	WO 98 07057 A (UNIV PENNSYLVANIA) 19 February 1998 see claims 1-9,15-32 see page 3, line 26 - page 5, line 5; figure 3	1

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

Inter[redacted]al Application No
PCT/[redacted]S 98/12295

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
CA 2188215 A	21-04-1997	JP 9171119 A	30-06-1997
EP 0615141 A	14-09-1994	US 5593621 A	14-01-1997
		WO 9404949 A	03-03-1994
EP 0606598 A	20-07-1994	BR 9305114 A	28-06-1994
		CA 2111761 A	19-06-1994
		CN 1103954 A	21-06-1995
		JP 8510763 T	12-11-1996
		WO 9415005 A	07-07-1994
WO 9807057 A	19-02-1998	US 5729645 A	17-03-1998

obtained by the polymerization of a sheathing monomer solution under the same conditions but not including the sheathing dopant; and (b) causing the sheathing monomer of the sheathing solution to polymerize within the polymerization container into a cylindrical sheathing tube at least partially transparent to light at at least one wavelength. The invention further provides a method for forming a gradient index plastic optical fiber. In the method, the gradient index plastic optical article is prepared, for example as described above, in the shape of a preform rod which is then be subjected to hot-drawing at a predetermined temperature and speed suitable to produce a fiber useful as an optical conductor. In one embodiment, the monomer of the sheathing solution and the monomer of the core solution are the same. Suitable monomers include those which form polymers that are substantially amorphous and capable of conducting light at the desired wavelength(s). For embodiments where the core polymer and the sheathing polymer are the same, when a core dopant is used it will be different from the sheathing dopant.

In another aspect gradient index plastic optical articles of the invention comprise: (a) a polymeric sheathing that is at least partially transparent to light at at least one wavelength including at least one sheathing polymer and at least one sheathing dopant, where the sheathing dopant has a refractive index which is less than that of the sheathing polymer; and (b) a polymeric core, coaxially disposed within the sheathing, including at least one core polymer and having a refractive index at the central axis of the core greater than that of the polymeric sheathing. In some embodiments, the polymeric core further includes at least one core dopant, the core dopant, when present, having a refractive index which is greater than that of the core polymer. In preferred embodiments, the core dopant has a concentration gradient in a specific direction.

In some embodiments, the plastic optical article is in the shape of a cylindrical preform rod. In other embodiments, the article is in the shape of a cylindrical fiber having an outer diameter preferably between about 0.1 millimeter and about 1 millimeter.

In yet another aspect, the invention involves a gradient index plastic optical article with a polymeric sheathing and a polymeric core. The polymeric sheathing is at least partially transparent to at least one wavelength of light and includes a sheathing polymer and a sheathing dopant, where the sheathing dopant has a refractive index which is less than that of an equivalent polymeric sheathing without the sheathing dopant. The polymeric core of the article is coaxially disposed within the sheathing, is at least partially transparent to at least

one wavelength of light and includes a core polymer. The polymeric core also has a gradient in refractive index in a specific direction.

In another aspect, the invention provides a method for forming a gradient index plastic optical article. The method involves forming a tube of polymeric sheathing material that is at least partially transparent to at least one wavelength of light from at least one polymerizable sheathing monomer and a sheathing dopant. A polymeric core that is at least partially transparent to at least one wavelength of light is then formed within the tube by filling the tube with a composition including at least one polymerizable core monomer and polymerizing the monomer. The polymeric core thus formed has a gradient in refractive index in a specific direction.

The invention also involves a gradient index plastic optical article which has a polymeric sheathing that includes a sheathing dopant.

In another aspect, the invention involves a gradient index plastic optical article with a polymeric sheathing and a polymeric core. The polymeric sheathing is at least partially transparent to at least one wavelength of light and includes a sheathing polymer. The polymeric core of the article is coaxially disposed within the sheathing, is at least partially transparent to at least one wavelength of light and includes a core polymer and a specific overall concentration of a core dopant that has a refractive index greater than that of the core polymer. Furthermore, the core dopant has a concentration gradient within the core in a specific direction. The polymeric sheathing of the article is constructed and arranged so that the difference in refractive indices between the central axis of the polymeric core and the polymeric sheathing exceeds the difference in refractive indices between the central axis of the polymeric core and the sheathing polymer.

In one aspect, the invention involves a gradient index plastic optical article with a polymeric sheathing and a polymeric core. The polymeric sheathing is at least partially transparent to at least one wavelength of light and includes a sheathing polymer. The polymeric core of the article is coaxially disposed within the sheathing, is at least partially transparent to at least one wavelength of light and includes a core polymer and a core dopant that has a refractive index greater than that of the core polymer. The core dopant is present in the polymeric core at a first overall concentration sufficient to create a difference in refractive indices between the central axis of the core and the sheathing of a desired value. In addition, the core dopant has a concentration gradient within the core in a specific direction. The

polymeric sheathing of the article is constructed and arranged so that the maximum service temperature of the article exceeds that of an equivalent article except having a sheathing comprised of only sheathing polymer and having a second overall core dopant concentration required to create a difference in refractive indices between the central axis of the core and the sheathing equal to the same desired value. In general, this increase in the permissible service temperature for articles manufactured according to the present invention having a particular difference in refractive indices between core and sheathing is enabled by the ability to use a lower amount of core dopant in order to create the desired difference in refractive indices.

In yet another aspect, the invention involves a gradient index plastic optical article with a polymeric sheathing and a polymeric core. The polymeric sheathing is at least partially transparent to at least one wavelength of light and includes a sheathing polymer. The polymeric core of the article is coaxially disposed within the sheathing, is at least partially transparent to at least one wavelength of light and includes a core polymer and a core dopant that has a refractive index greater than that of the core polymer. The core dopant is present in the polymeric core at a first overall concentration sufficient to create a difference in refractive indices between the central axis of the core and the sheathing of a desired value. Furthermore, the core dopant has a concentration gradient within the core in a specific direction. The polymeric sheathing of the article is constructed and arranged so that at least one wavelength of light is conducted by the article with less attenuation than by an equivalent article except having a sheathing comprised of only sheathing polymer and having a second overall core dopant concentration required to create a difference in refractive indices between the central axis of the core and the sheathing equal to the same desired value.

In one aspect, the invention involves an optical preform article. The preform includes a polymeric sheathing, which is at least partially transparent to at least one wavelength of light and has a refractive index of a first value at that wavelength. The polymeric sheathing includes a sheathing polymer and a plasticizer. The preform also includes a polymeric core, which includes a core polymer, that is coaxially disposed within the sheathing and is at least partially transparent to the same wavelength(s) of light as the polymeric sheathing, and which has a refractive index of a second value at the central axis of the core at that wavelength. The preform is fabricated so that the second value of refractive index (i.e. at the central axis of the polymeric core) exceeds the first value (i.e. of the sheathing).

In another aspect, the invention involves a method for making a plurality of optical

preform articles. The method involves forming a plurality of polymeric sheathings, each of which includes a sheathing polymer, is at least partially transparent to at least one wavelength of light, and has a refractive index of a first value at that wavelength. The method also involves forming a plurality of polymeric cores, each of which includes a core polymer, that is coaxially disposed within the sheathing and is at least partially transparent to the same wavelength(s) of light as the polymeric sheathing, and which has a refractive index of a second value at the central axis at that wavelength that exceeds the first value of the sheathing. The region of contact between the sheathings and the cores thus formed defines a plurality of interfaces, with essentially all of the plurality of interfaces being essentially free of visible bubbles. In other words, the invention enables a large number of preforms to be made, each of which is essentially free of visible bubbles along its entire "as polymerized" length (e.g. without cutting the preform after polymerization).

In another embodiment, the invention involves an optical preform article. The preform includes a polymeric sheathing, which includes a sheathing polymer, that is at least partially transparent to at least one wavelength of light and has a refractive index of a first value at that wavelength. The preform also includes a polymeric core that is coaxially disposed within the sheathing and is at least partially transparent to the same wavelength(s) of light as the polymeric sheathing, and which has a refractive index of a second value at the central axis of the core at that wavelength that exceeds the first value of the sheathing. The polymeric core includes a core polymer and a core dopant having a refractive index which is greater than that of the core polymer. The core dopant is present in the polymeric core at a specified overall concentration. Furthermore, the second value of refractive index (i.e. of the central axis of the polymeric core) exceeds the first value (i.e. of the polymeric sheathing) by at least 0.01, with the specified overall core dopant concentration not exceeding 12 %wt.

In another aspect, the invention involves a plastic optical article. The article comprises a polymeric sheathing, which is at least partially transparent to at least one wavelength of light and a polymeric core, coaxially disposed within the sheathing, which is also at least partially transparent to the same wavelength of light. The polymeric sheathing includes a sheathing polymer, and the polymeric core includes a core polymer and a core dopant that has a refractive index greater than that of the core polymer. The refractive index of the central axis of the polymeric core has a value at the wavelength of light mentioned above that exceeds the refractive index of the polymeric sheathing at the same wavelength by

at least 0.01. Furthermore, the maximum service temperature of the article is at least 40 degrees C, preferably 45 degrees C, and more preferrably 50 degrees C.

In yet another aspect, the invention provides a method for making a gradient plastic optical fiber. The method involves first forming a polymeric preform rod comprising a polymeric sheathing and a polymeric core coaxially disposed within the sheathing that has a gradient in refractive index in a specified direction. The preform is then hot-drawn at a rate of at least 3 m/min, preferably at least 4 m/min, and more preferably, at least 5 m/min, into a fiber. The fiber thus produced conducts at least one wavelength of light with an attenuation less than 500 dB/km.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 shows one embodiment of a gradient index plastic optical article according to the invention;

Figure 2 is a graph showing the relationship between the transmission loss (attenuation) and wavelength of light for an optical fiber according to the invention; transmission loss at 650 nm was approximately 140 dB/km demonstrating that the optical fiber had a high level of transparency.

DETAILED DESCRIPTION OF THE INVENTION

The features and other details of the invention will now be more particularly described and pointed out in the detailed description and examples below. It will be understood that the particular embodiments of the invention are shown by way of illustration only and are not intended to act as limitations of the invention. The principle features of this invention can be employed in various embodiments not specifically described herein without departing from the spirit and scope of the invention.

In one aspect, the invention provides a method for forming a gradient index plastic optical article including the steps of: (a) forming a tube of polymeric sheathing material that is at least partially transparent to light at at least one wavelength by: (i) placing into a polymerization container a sheathing solution including at least one polymerizable sheathing monomer and a plasticizer and/or dopant; and (ii) causing the sheathing monomer of the

container can be any shape which when rotated about its own axis creates a sheathing tube with an annular cylindrical shape. The preferred shape of the container is a circular cylinder preferably with dimensions suitable for hot-drawing into an optical fiber, for example, with an inner diameter between 0.25 and 2 inches. The centrifugal force resulting from the rotation of the polymerization container will cause the resulting polymer to form a tube of sheathing material or a sheathing tube within the polymerization container. Rotation can be accomplished, for example, by spinning the container.

The amount of sheathing-forming solution placed in the polymerization container can be determined based upon the ratio of the thickness of the sheathing wall to the distance between the opposing interior walls of the sheathing which is desired. This ratio will depend upon the cost of materials and the end use of the optical article.

Alternatively, the sheathing can also be prepared by extrusion of the sheathing polymer, together with any additives such as plasticizers and/or dopants, into tubular shapes using extrusion methods which are well known to those of skill in the art. The outer and inner shape of the sheathing using this method will be dictated by the shape of the extrusion dye. The extruded sheathing will then serve as the container into which the core-forming solution will be added and allowed to polymerize.

The polymerizable sheathing monomer can be any monomer or mixture of monomers which upon polymerization yields substantially amorphous and transparent polymeric materials. Preferably, the polymeric materials of the sheathing are at least partially soluble in the monomer present in the core-forming solution and exhibit a suitable miscibility with the sheathing dopant and/or plasticizer.

Polymerizable monomers suitable for use in this invention include, but are not limited-to, for example, methacrylate monomers such as branched and unbranched C_1-C_{10} alkyl methacrylates, for example, methyl methacrylate, ethyl methacrylate, n-propyl methacrylate, n-butyl methacrylate, n-hexyl methacrylate, isopropyl methacrylate, isobutyl methacrylate, tert-butyl methacrylate; halogenated methacrylates, such as 2,2,2-trifluoroethyl methacrylate; 4-methyl cyclohexyl methacrylate, cyclohexyl methacrylate, furfuryl methacrylate 1-phenylethyl methacrylate, 2-phenylethyl methacrylate, 1-phenylcyclohexyl methacrylate, benzyl methacrylate and phenyl methacrylate; acrylate monomers such as, methyl acrylate, ethyl acrylate, n-butyl acrylate, benzyl acrylate, 2-chloroethyl acrylate, methyl-α-chloro acrylate, 2,2,3,3-tetrafluoropropyl-α-fluoro acrylate, and 2,2,2-trifluoroethyl

Claims

1. A gradient index plastic optical article comprising:

a polymeric sheathing, which is at least partially transparent to light at at least one wavelength, including a sheathing polymer and a sheathing dopant, the sheathing dopant having a refractive index which is less than that of the an equivalent polymeric sheathing without the sheathing dopant; and

a polymeric core, including a core polymer, coaxially disposed within said sheathing, said core being at least partially transparent to light at at least one wavelength and having a gradient in refractive index in a specific direction.

2. The article of claim 1, wherein said sheathing dopant lowers the refractive index of the polymeric sheathing by at least 0.0005 compared to an equivalent sheathing without said sheathing dopant.

3. The article of claim 1, wherein said sheathing dopant is present in the polymeric sheathing at an overall concentration less than 35 %wt.

4. The article of claim 1, wherein said sheathing dopant is present in the polymeric sheathing at an overall concentration less than 20 %wt.

5. The article of claim 1, wherein said sheathing dopant is present in the polymeric sheathing at an overall concentration less than 15 %wt.

6. The article of claim 1, wherein the interface between said polymeric sheathing and said polymeric core is essentially free of visible bubbles.

7. The article according to claim 1, wherein said polymeric sheathing and said polymeric core are both at least partially transparent to the same at least one wavelength of light.

8. The article of claim 1, wherein said polymeric core further includes a core dopant having a refractive index which is greater than that of an equivalent polymeric core without the core dopant.

39. The method of claim 37, wherein said energy is in the form of heat.

40. The method of claim 32, wherein said polymerization container is rotated during step (c).

41. The method of claim 31, wherein said polymerizable sheathing monomer and said polymerizable core monomer are different.

42. The method of claim 31, wherein said polymerizable sheathing monomer and said polymerizable core monomer are the same.

43. The method of claim 42, wherein the polymerizable monomer is methyl methacrylate.

44. The method of claim 31 further comprising the step of hot-drawing the article formed after the completion of step (b) at a predetermined temperature and speed to form a gradient index optical fiber.

45. A gradient index plastic optical article having a polymeric sheathing that includes a sheathing dopant.

46. A gradient index plastic optical article comprising:

a polymeric sheathing, which is at least partially transparent to light at at least one wavelength, including a sheathing polymer; and

a polymeric core coaxially disposed within said sheathing, which is at least partially transparent to light at at least one wavelength, including a core polymer and a specific overall concentration of a core dopant having a refractive index greater than that of the core polymer, said core dopant having a concentration gradient within the core in a specific direction;

said polymeric sheathing being constructed and arranged so that a difference in refractive indices between the central axis of said polymeric core, having said overall concentration of core dopant, and said polymeric sheathing exceeds a difference in refractive

indices between said central axis of said polymeric core. having said overall concentration of core dopant, and said sheathing polymer.

47. The article of claim 46, wherein said overall concentration of core dopant is zero.

48. The article of claim 46, wherein said polymeric sheathing includes a sheathing dopant having a refractive less than that of said sheathing polymer.

49. The article of claim 46, wherein the refractive index at the central axis of said polymeric core is greater than the refractive index of said polymeric sheathing, where said article conducts light at at least one wavelength with an attenuation less than 500 dB/km.

50. A gradient index plastic optical article comprising:

a polymeric sheathing, which is at least partially transparent to light at at least one wavelength, including a sheathing polymer; and

a polymeric core coaxially disposed within said sheathing, which is at least partially transparent to light at at least one wavelength, comprising a core polymer and a core dopant having a refractive index greater than that of the core polymer and present at a first overall concentration sufficient to create a difference in refractive indices between the central axis of the core and the sheathing of a desired value, said core dopant having a concentration gradient within the core in a specific direction;

said polymeric sheathing being constructed and arranged so that the maximum service temperature of the article exceeds that of an equivalent article except having a sheathing comprised only of sheathing polymer and having a second overall core dopant concentration required to create a difference in refractive indices between the central axis of the core and the sheathing equal to said desired value.

51. The article of claim 50, wherein said overall concentration of core dopant is zero and where said polymeric core has a refractive index gradient within the core in a specific direction.

52. The article of claim 50, wherein said polymeric sheathing includes a sheathing dopant having a refractive less than that of said sheathing polymer.

53. The article of claim 50, wherein the refractive index at the central axis of said polymeric core is greater than the refractive index of said polymeric sheathing, where said article conducts light at at least one wavelength with an attenuation less than 500 dB/km.

54. A gradient index plastic optical article comprising:

a polymeric sheathing, which is at least partially transparent to light at at least one wavelength, including a sheathing polymer ; and

a polymeric core coaxially disposed within said sheathing, which is at least partially transparent to light at at least one wavelength, including a core polymer and a core dopant having a refractive index greater than that of the core polymer and present at a first overall concentration sufficient to create a difference in refractive indices between the central axis of the core and the sheathing of a desired value, said core dopant having a concentration gradient within the core in a specific direction;

said polymeric sheathing being constructed and arranged so that said light at at least one wavelength is conducted by the article with less attenuation than by an equivalent article except having a sheathing comprised only of sheathing polymer and having a second overall core dopant concentration required to create a difference in refractive indices between the central axis of the core and the sheathing equal to said desired value.

55. The article of claim 54, wherein said overall concentration of core dopant is zero.

56. The article of claim 54, wherein said polymeric sheathing includes a sheathing dopant having a refractive less than that of said sheathing polymer.

57. The article of claim 54, wherein the refractive index at the central axis of said polymeric core is greater than the refractive index of said polymeric sheathing, where said article conducts light at at least one wavelength with an attenuation less than 500 dB/km.

58. A plastic optical preform article comprising:

a polymeric sheathing, which is at least partially transparent to light at at least one wavelength and possesses a refractive index of a first value at said at least one wavelength, including a sheathing polymer and a plasticizer; and

a polymeric core, coaxially disposed within said sheathing, which is at least partially transparent to light at at least one wavelength, possesses a refractive index of a second value at the central axis of the core at said at least one wavelength, and includes a core polymer; said second value of refractive index exceeding said first value.

59. The article of claim 58, wherein the polymeric core has a refractive index gradient within the core in a specific direction.

60. The article of claim 58, wherein said preform can be formed into an essentially cylindrical optical fiber having an outer diameter less than 1 millimeter by extrusion.

61. The article of claim 60, wherein said fiber conducts light at at least one wavelength with an attenuation less than 500 dB/km.

62. The article of claim 58, wherein said preform can be formed into an essentially cylindrical optical fiber having an outer diameter less than 1 millimeter by hot-drawing.

63. The article of claim 62, wherein said fiber conducts light at at least one wavelength with an attenuation less than 500 dB/km.

64. The article of claim 63, wherein said fiber is hot-drawn from said rod at a drawing speed of at least 3 m/min.

65. The article of claim 63, wherein said fiber is hot-drawn from said rod at a drawing speed of at least 5 m/min.

66. The article of claim 58, wherein said plasticizer acts as a sheathing dopant having a refractive index which is less than that of said sheathing polymer.

67. The article of claim 58, when said polymeric core further includes a core dopant.

68. The article of claim 58, wherein said sheathing polymer and said core polymer are formed from the same polymerizable monomer.

69. The article of claim 68, wherein the polymerizable monomer is a perfluorinated monomer which yields an amorphous perfluorinated polymer upon polymerization.

70. The article of claim 58, wherein said sheathing polymer and said core polymer are formed from the different polymerizable monomers.

71. The article of claim 70, wherein the polymerizable monomer forming the sheathing polymer is a perfluorinated monomer which yields an amorphous perfluorinated polymer upon polymerization.

72. A method for making a gradient index plastic optical fiber comprising:

forming a polymeric preform rod comprising a polymeric sheathing and a polymeric core coaxially disposed within said sheathing, said polymeric core having a gradient in refractive index in a specific direction; and

hot-drawing said rod at a draw rate of at least 3 m/min into a fiber that conducts light of at least one wavelength with an attenuation less than 500 dB/km.

73. A plastic optical preform article comprising:

a polymeric sheathing, which is at least partially transparent to light at at least one wavelength, possesses a refractive index of a first value at said at least one wavelength, and includes a sheathing polymer; and

a polymeric core, coaxially disposed within said sheathing, which is at least partially transparent to light at at least one wavelength, possesses a refractive index of a second value at the central axis of the core at said at least one wavelength, and includes a core polymer and a core dopant having a refractive index greater than that of the core polymer and present at a specified overall concentration;

said second value of refractive index exceeding said first value by at least 0.01 at said at least one wavelength, with said specified overall core dopant concentration not exceeding 12 %wt.

74. A plastic optical article comprising:

a polymeric sheathing, which is at least partially transparent to light at at least one wavelength, possesses a refractive index of a first value at said at least one wavelength, and includes a sheathing polymer; and

a polymeric core, coaxially disposed within said sheathing, which is at least partially transparent to light at at least one wavelength, possesses a refractive index of a second value at the central axis of the core at said at least one wavelength, and includes a core polymer and a core dopant having a refractive index greater than that of the core polymer;

said second value of refractive index exceeding said first value by at least 0.01 at said at least one wavelength, and the operating temperature of the article being at least 40 degrees C.